Revisiting geochemical controls on patterns of carbonate deposition through the lens of multiple pathways to mineralization†

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The carbonate sedimentary record contains diverse compositions and textures that reflect the evolution of oceans and atmospheres through geological time. Efforts to reconstruct paleoenvironmental conditions from these deposits continue to be hindered by the need for process-based models that can explain observed shifts in carbonate chemistry and form. Traditional interpretations assume minerals precipitate and grow by classical ion-by-ion addition processes but are unable to reconcile a number of unusual features contained in Proterozoic carbonates. The realization that diverse organisms produce high Mg carbonate skeletal structures by non-classical pathways involving amorphous intermediates raises the question of whether similar processes are also active in sedimentary environments. This study examines the hypothesis that non-classical pathways to mineralization are the physical basis for some of the carbonate morphologies and compositions observed in natural and laboratory settings. We designed experiments with a series of different solution Mg : Ca ratios and saturation environments to investigate the effects on carbonate phase, Mg content, and morphology. Our observations of diverse carbonate mineral compositions and textures suggest geochemical conditions bias the mineralization pathway by a systematic relationship to Mg : Ca ratio and the abundance of carbonate ions. Environments with low Mg levels produce calcite crystallites with 0–12 mol% MgCO₃. In contrast, the combination of high initial Mg : Ca and rapidly increasing saturation opens a non-classical pathway that begins with extensive precipitation of an amorphous calcium carbonate (ACC). This phase slowly transforms to aggregates of very high Mg calcite nanoparticles whose structures and compositions are similar to natural disordered dolomites. The non-classical pathways are favored when the local environment contains sufficient Mg to inhibit calcite growth through increased solubility—a thermodynamic factor, and achieves saturation with respect to ACC on a timescale that is shorter than the rate of aragonite nucleation—a kinetic factor. Aragonite is produced when Mg levels are high but saturation is insufficient for ACC precipitation. The findings provide a physical basis for anecdotal claims that the interplay of kinetic and thermodynamic factors underlies patterns of carbonate precipitation and suggest the need to expand traditional interpretations of geological carbonate formation to include non-classical pathways to mineralization.

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The precipitation of carbonate minerals to form sediments and sedimentary rocks provides our most comprehensive proxy record of global environmental change over the course of Earth history. Of particular interest are the ancient carbonate rocks of the Proterozoic. Reaching backward in time more than two billion years, this unique interval of Earth history marks the evolution of our planet from an inorganic to a biological world. The era is characterized by deposition of extensive carbonate sediments with unusual textures and mineral chemistries. Many of the features are rarely seen again in the geologic record and are distinct from the biological calcification of skeletal structures that dominated carbonate precipitation in the Phanerozoic.¹ These shifts in carbonate phases, compositions, and textures are broadly agreed to reflect important changes in the interactions between physical and biological processes.² However, we have only an incomplete picture of the mechanistic basis for the diverse patterns of carbonate mineral precipitation recorded in these deposits. Therefore, the mineralization processes that regulate distributions of trace elements and isotopes within carbonate structures—the proxies of greatest paleoenvironmental interest—remain crucial targets of research.

Calcite and aragonite are the most important polymorphs of calcium carbonate (CaCO_3) that form in modern seawater.^{3–6} Also of considerable interest is dolomite, a Mg-rich carbonate ($\text{CaMg}(\text{CO}_3)_2$) that is widely found in ancient sediments but today seen only in restricted marine environments.⁷ While equilibrium thermodynamics is thought to have the principal control on geological mineral precipitation, kinetic factors are also known to play important roles in the formation of these different phases. For example, the long-standing “dolomite problem” refers to observations that dolomite only very stubbornly precipitates at low temperature despite being significantly oversaturated in seawater as compared to calcite and aragonite.⁷ Similarly, seawater is less supersaturated with respect to aragonite than to calcite, yet aragonite tends to precipitate first from seawater due to kinetic inhibition of calcite.^{4,5,8}

Until recently, most interpretations of how carbonate minerals form in sedimentary environments were based upon the assumption that mineralization occurs by the ion-by-ion attachment of solutes to the mineral surfaces by the classical terrace–ledge–kink (TLK) model of crystal growth.^{9,10,11} While TLK theory has provided the foundation for designing and interpreting many studies of calcite, a long-standing enigma is the inability of this growth process to produce low temperature carbonates with more than 10–12 mol% Mg.^{3,12,13} Moreover, *in situ* observations confirm that calcite growth by classical step propagation becomes fully inhibited at Mg levels far below those measured in seawater, thus precluding the possibility that very high Mg carbonates, such as protodolomite, can form by this pathway at low temperature.^{8,14,15}

The biomineralization community has faced a similar dilemma regarding the processes by which organisms exert species-specific controls on the Mg content of carbonate skeletons. For example, the coccoliths of calcifying algae contain approximately 0–3 mol% MgCO_3 (low Mg calcite, LMg calcite)¹⁶ while coralline red algae contain 5–15 mol% MgCO_3 (high Mg calcite, HMg calcite).¹⁷ In contrast, certain echinoderm species readily produce complex calcified biominerals with as much as 30 mol% MgCO_3 ¹⁸ while the teeth of sea urchins can contain up to 50 mol%.¹⁹ It is now recognized that these very high Mg calcite (VHMg calcite) structures form by a two-stage mineralization process that begins with the accumulation of amorphous calcium carbonate (ACC) in a localized environment^{20–23} followed by its transformation to 5–100 nm nanoparticles. The resulting crystals can have significant crystallographic co-alignment at the nanoscale to produce the complex superstructures we know as skeletal biominerals.^{24–27}

Studies of synthetic inorganic materials show similar processes can produce crystalline aggregates of co-aligned nanoparticles—often referred to as

mesocrystals—with a wide variety of mineral chemistries.^{28,29} Details vary, but the conditions required for mesocrystal formation are generally characterized by 1) high supersaturation conditions that favor extensive nucleation; 2) the presence of inhibitors that limit crystallite growth; and 3) quiescent environments that allow interaction potentials of particle surfaces to favor aggregation along preferred orientations. Studies also demonstrate that organic and some polymeric species can mediate crystal–crystal interactions during mesocrystal formation.^{28–30}

Emerging concepts from biomineral and synthetic materials studies of the amorphous-to-mesocrystal pathway raise the question of whether a similar process could be the missing link to interpreting the origins of some high and very high Mg carbonates. The influence of magnesium is of particular interest because the ratio of Mg : Ca in seawater has varied over geologic history⁴ and Mg slows the growth rate of carbonate minerals. However, few experiments have investigated this influence while monitoring the pathway to mineral formation. Two recent studies show the Mg content of ACC can attain (and exceed) the composition range of VHMg calcite and dolomite.^{31,32} Those studies, however, cannot provide insights into the nature of the final crystalline products. Here we tested the hypothesis that the interplay of Mg : Ca ratio and the abundance of carbonate ion regulate the pathway to carbonate formation. To investigate this idea, we designed two calcification environments that varied the abundance of carbonate ion and Mg : Ca of the solution. By monitoring the products that formed, we found composition and morphological evidence for three pathways to calcite formation. The relations also suggest a plausible explanation for the formation of calcite *versus* aragonite at low temperatures.

2 Experimental

The saturation state of a solution with respect to ACC and calcite is determined by the relations

$$K_{\text{sp,calcite}} = (a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}) / a_{\text{CaCO}_3, \text{calcite}} \quad (1)$$

$$K_{\text{sp,ACC}} = (a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}) / a_{\text{CaCO}_3, \text{ACC}} \quad (2)$$

where a_i is the chemical activity of an ion or solid and the solubility products are $K_{\text{sp,calcite}} = 10^{-8.43}$ and $K_{\text{sp,ACC}} = 10^{-6.39}$,³³ respectively. Thus, the reported K_{sp} of pure ACC is approximately 100× greater than calcite. If the ACC solubility value is correct, an ACC-saturated solution with equivalent activities of Ca^{2+} or CO_3^{2-} contains approximately 10× more Ca^{2+} and 10× more CO_3^{2-} than a calcite-saturated solution.

2.1 Mineralization

Solutions were prepared using reagents of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Sigma Aldrich, 99+%) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma Alrich, 99%). Most experiments were conducted with Ca^{2+} concentrations of 10 mM and Mg levels were set to obtain starting molar ratios of Mg : Ca = 0.0 to 6.0. Additional experiments were conducted at $[\text{Ca}^{2+}] = 25$ mM and, again, Mg levels were set accordingly.

Supersaturation was achieved using two established methods. For the ammonium carbonate diffusion method, 10 g of $(\text{NH}_4)_2\text{CO}_3$ (Sigma Aldrich) was dissolved in 20 mL distilled deionized water to provide the carbonate source.^{31,34–37} After adding the salt solutions described above to six replicate vessels that contained silica glass substrates or carboxylated surfaces prepared by standard methods (Wallace *et al.*, 2009) using MUA on gold. The solutions were exposed to the ammonium carbonate source and incubated in closed vessels at 40 °C and 100% humidity. The ammonium

carbonate solutions were removed after 1 day and the precipitates were removed and washed with anhydrous ethanol after 3 days.

A second method used a batch approach to mix solutions of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and NaHCO_3 to produce reactants with lower carbonate levels and $\text{pH} = 8.5$. Initial Ca^{2+} concentrations were 10 mM. To keep the initial saturation state equivalent for all batch experiments, $[\text{HCO}_3^-]$ varied from 12 to 30 mM depending on solution $\text{Mg} : \text{Ca}$, which ranged from 0.0 to 6.0. Solutions were mixed in 3 mL wells containing silica glass substrates for precipitate collection. After 6 days at 25 °C, the substrates were removed and washed with anhydrous ethanol.

For both methods, parallel experiments were conducted to monitor pH and decreases in the solution Mg^{2+} and Ca^{2+} concentrations by sampling 2 mL from the replicates while also while observing the onset and progression of mineralization using an optical microscope. Solutions for chemical analysis were filtered through 0.2 μm nylon membranes (Whatman) and analyzed for Mg and Ca by inductively coupled plasma atomic emission spectrometry (Spectro ARCOS SOP).

2.2 Preparation of Coorong dolomite

Disordered dolomites from the Coorong Lakes, South Australia were sonicated in 30% peroxide for two hours, centrifuged for 10 min, and washed with ethanol. The samples were dispersed on substrates for analysis.

2.3 X-Ray diffraction (XRD)

For each treatment, three replicate samples were analyzed on a PANalytical X'PERT PRO with $\text{Cu-K}\alpha_1$ radiation operated at 45 kV and 40 mA from 20°–60° 2 θ at scan speeds of 0.02° sec⁻¹. MgCO_3 compositions were determined using a linear correlation³⁹ of peak position to composition. All sample (104) peaks were corrected by the silicon (111) peak at 28.439° 2 θ using a powdered silicon internal standard (NIST 640D), deposited by ethanol dispersion. Noting that structural considerations such as lattice disorder are convoluted into (104) peak position, especially in a disordered material, a recent study of calcites (0–50 mol% MgCO_3) found measurements using a linear correlation represent a lower bound on MgCO_3 content.⁴⁰

2.4 Electron microscopy

SEM images were collected using a FEI Helios 600 Nanolab operated at 5 kV accelerating voltage. TEM samples were prepared by established focused ion beam (FIB) methods⁴¹ on a FEI Helios 600 Nanolab. TEM selective area electron diffraction (SAED) patterns and dark field images were collected on a Philips EM420 operated at 120 kV.

3 Results

3.1 Morphology

For the ammonium carbonate diffusion method, visible precipitation began in the Mg-free experiments that contained the lower concentration of calcium (10 mM) with the formation of euhedral calcite crystallites (Fig. 1A). At the higher calcium level (25 mM), ACC was observed for the first few minutes of the experiment. For both conditions, any visible ACC underwent rapid dissolution to become a source of ions for the growing crystallites. The resulting crystallites exhibited a rhombohedral morphology, without evidence of polycrystals, indicating growth by step propagation. Calcite crystallites also formed, albeit more slowly, from solutions with an initial $\text{Mg} : \text{Ca}$ level of 1.0 to produce the elongated ‘birdseed’ morphology (Fig. 1B) previously reported for Mg-bearing calcites.^{36,37,42}

Fig. 1 Systematic changes in calcite morphology indicate shifts in the predominant mineralization processes as step growth becomes progressively inhibited by Mg concentrations in solution. (A) Mg : Ca = 0. Crystallites grow by a classical step growth process and exhibit the rhombohedral morphology typical of the pure calcite system; (B) Mg : Ca = 1. Elongated birdseed crystallites that also express (104) facets; (C) Mg : Ca = 2.0. Crystallites that form at higher Mg levels are elongated assemblages of small calcite particles (inset); (D, E) onset of transition at Mg : Ca = 3.0 produces a mixture of morphologies with high Mg calcite spherules and aggregates of very high Mg calcite nanoparticles, respectively. (F) Mg : Ca = 4.0; (G) Mg : Ca = 5.0; (H) Mg : Ca = 6.0. For all Mg : Ca levels, films of ACC transform into similar low-relief aggregates of very high Mg calcite nanoparticles aggregates that exhibit a botryoidal texture. All scale bars = 20 microns.

A significant morphological change was seen in the calcite crystallites that form from solutions that began with a Mg : Ca ratio of 2.0 to 3.0. After the extensive formation of ACC particles on the surface, calcite crystallites developed with dumbbell and spherulitic morphologies, respectively (Fig. 1CDE). The structures are regular but lack evidence of faceting seen at the lower Mg : Ca solutions. The dumbbell structures had the appearance of being comprised of smaller particles with like morphology (inset Fig. 1C). Raman spectroscopy confirmed that all of the crystallites were calcite. At the higher Mg : Ca = 3.0, the spherulitic calcites are accompanied by a small proportion of disc-shaped aggregates that marked the beginning of a transition to a different mineralization process (Fig. 1E).

When the initial Mg : Ca levels were ≥ 4.0 , a third type of calcite morphology was observed (Fig. 1FGH). Precipitation began with the accumulation of high Mg ACC onto the substrate as a continuous sheet, without evidence of crystallites (Fig. 2A). The ACC layer subsequently transformed to circular, low relief aggregates of calcite nanoparticles (Fig. 2BC). As aggregates developed, the surrounding ACC was depleted (Fig. 2BC) and the calcite developed with a distinctive botryoidal (anisotropic and radial) texture without macroscopic evidence of external crystallographic control (Fig. 2D). TEM dark field images, however, showed significant co-alignment of the constituent nanoparticles within the aggregates (Fig. S1†). The morphology of these calcites was independent of solution Mg : Ca level (Fig. 1FGH) but their rate of transformation, significantly slowed with increasing Mg : Ca ratio of the initial solution. For example, solutions with a Mg : Ca ratio of 4.0 and 6.0 underwent the ACC to calcite transformation in approximately 1 day and 3 days, respectively. Allowing the experiments to continue after all of the ACC had transformed to calcite, we observed the formation of late stage aragonite. ACC and aragonite were not observed to co-exist in any of the experiments.

3.2 Composition

Measurements of the corresponding precipitate compositions showed the Mg content of ACC was linearly dependent upon solution Mg : Ca ratio (Fig. 3A) as

Fig. 2 Under extreme conditions, ACC forms as a sheet that transforms into very high Mg calcite. All scale bars = 25 microns. (A) Typical morphology after 5 h for initial Mg : Ca of 5.0 shows a continuous film of ACC. (B) After 12 h, the very high Mg calcite begins to form as circular discs that develop from the ACC film. (C) At an intermediate stage (24 h), these regions evolve into low relief aggregates of very high Mg calcite aggregates. The surrounding ACC is depleted and appears as discrete particles that reveal the underlying glass substrate. (D) Late stage (3 days) very high Mg calcite aggregates.

reported previously.^{31,32} Comparisons of the calcite compositions and the fractionation patterns of the calcites that transformed from this metastable intermediate provided independent evidence for multiple mineralization pathways. Field (1) shows that when solutions have low Mg : Ca levels, the ACC and euhedral calcites that formed have the same Mg content, and thus, the same fractionation within experimental errors. Our measurements of 0–12 mol % MgCO_3 in the calcite crystallites are consistent with reports for classical step growth.¹³

At the higher Mg : Ca levels that correspond to Field (2), the ACC transformed to HMg calcites of 10–20 mol% MgCO_3 . Note that these levels of Mg are lower than what was measured for its amorphous precursor. Thus, the transformation process reduced the Mg content in the calcite by up to 10%. Qualitative observations showed the amount and size of crystallites decreased in parallel with an increasing Mg content of the calcite that formed. This is consistent with measurements showing that Mg incorporation slows the rate of calcite growth by the step propagation process.⁸ The change in kinetics is a consequence of the higher solubility of the Mg–calcite solid solution products ($\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3$), a thermodynamic effect.⁸

At Mg : Ca ratios ≥ 3 , Field (3) shows that the highest Mg ACC transformed to a VHMg calcite that contained 35–40 mol % MgCO_3 . The compositions exhibit a plateau in Mg content without evidence of fractionation with the composition of the solution or its amorphous precursor. While our estimates of the higher Mg contents may contain as much as 2% error (*e.g.* experimental), the amounts of Mg in the crystallites are nonetheless $>2\times$ greater than measurements for the crystallites in Field (2). Significantly, values of up to 40 mol% MgCO_3 are within the composition range of disordered dolomites.⁴³

Fig. 3 Pathway to mineralization influences calcite composition. (A) The composition of ACC exhibits a linear dependence upon initial Mg : Ca ratios as reported previously.^{31,32} The composition of calcites that transform from the ACC shift in composition according to Mg : Ca levels: for solutions with low Mg : Ca levels (1), the ACC transformation produces calcites with similar compositions. Measurements of 0–12 mol % MgCO₃ are consistent with studies for classical step growth. At higher Mg : Ca levels (2), Mg is excluded during the ACC transformation to produce calcite with a lower Mg content than its amorphous precursor. The calcites that form from ACC at these highest Mg : Ca levels (3) exhibit a plateau in Mg content. For the conditions of these experiments, these VHMg calcites contain approximately 35–40 mol % MgCO₃. Calcites that transform from ACC in solutions that contain two concentrations (0.025 M and 0.05 M) of (B) the composition of calcites that form from ACC in the presence of aspartate; and (C) sulfate solutions show similar compositions. Precipitation onto carboxyl-functionalized substrates gives similar trends (Fig. S3†)

Measurements of chemical composition changes during the mineralization process showed the evolution of total solution Mg, Ca and Mg : Ca ratio over the course of experiments conducted at initial solution Mg : Ca = 2.0 and 4.0 (Fig. 4AB). A maximum pH of 10 was reached during the course of the experiments. Recall that these conditions produced HMg calcite crystallites and VHMg calcite nanoparticle aggregates, respectively. As seen in Fig. 4AB, sharp increases occurred in solution Mg : Ca ratios during the first few hours until becoming approximately constant (Fig. 4AB).

Fig. 4 Measurements of solution chemistry during precipitation for experiments conducted at (A) initial Mg : Ca = 2 and (B) initial Mg : Ca = 4. The data show minimal changes in total Mg compared to the large decrease in calcium concentration. Thus, both solutions acquire very high Mg : Ca levels as precipitation proceeds. For Mg : Ca solutions = 2, the rapid decrease in Ca^{2+} concentration to approximately 0.5 mM is indicative of very early precipitation of Mg calcite. In contrast, solutions with initial Mg : Ca = 4 show that total Ca concentration is maintained at the higher value of 0.8 mM for 16 h, indicating the inhibition of calcite formation and the stability of ACC. Dashed line indicates stoichiometric solubility of ACC at 40 °C.³³

For experiments at $\text{Mg} : \text{Ca} \leq 3.0$, Fig. 3ABC shows the Mg content of crystallites that formed is dependent upon initial solution composition. This suggests, in Field (2), Mg levels are set by the initial, or very early solution composition (*e.g.* Fig. 4A). In contrast, in Field (3), experiments conducted at $\text{Mg} : \text{Ca} = 4.0$ showed Mg content is not dependent upon initial solution composition. In this case, the nanoparticle calcite is not transformed from ACC until several hours after the start of the experiment when Mg : Ca levels approached the long asymptote of the solution conditions ($\text{Mg} : \text{Ca} = 30\text{--}40$) at the time of transformation (Fig. 4B). This suggests the ‘compositional gap’ (Fig. 3ABC) between Fields (2) and (3) is an artifact of changing solution conditions and delay of calcite formation in Field (3).

Additional experiments investigated the influence of organic and inorganic constituents that are commonly found in biological and sedimentary environments on mineralization by these processes. The acidic aspartate (Asp , $\text{C}_4\text{H}_6\text{NO}_4^-$) and other carboxylated biomolecules are implicated in promoting calcification and Mg uptake^{22,31} while studies have debated the role of sulfate (SO_4^{2-}) as both an inhibiting⁴⁴ and catalyzing agent⁴⁵ in the formation of high Mg carbonates. For the conditions of these experiments, we find that neither of these molecules significantly influenced composition (Fig. 3B and C, respectively) or morphology (Fig. S2†).

Because the single Asp residue has small effects on mineralization compared to larger carboxylated macromolecules^{15,22} found in eutrophic environments, further studies of biomolecule effects are needed. Parallel experiments conducted on the carboxyl-terminated substrates (Fig. S3†) produced the same composition and texture trends as seen in the additive-free experiments.

4 Discussion

Observations of distinctive patterns in calcite morphology (Fig. 1) and composition (Fig. 3) suggest an interplay between Mg content—an inhibitor to step growth—and the supersaturation—which has a primary control on rates of nucleation and step growth. Low levels of Mg in solution allow crystallites of calcite to nucleate and grow by the classical process, including those solutions with saturation states that exceed ACC solubility. As Mg is introduced to solution and the growing calcite incorporate progressively higher levels of this ion, the rate of growth slows.^{8,14} Calcite compositions reflect the initial Mg : Ca conditions and may be related by a fractionation coefficient, shown in Fields (1) and (2) of Fig. 3A. This interpretation is consistent with studies that estimate a Mg : Ca ratio of 1.0 to 2.0 as the threshold for inhibiting calcite growth^{8,14,15,46} and the transition to aragonite precipitation.^{4,47}

In contrast, the pathway to producing VHMg calcite is favored when Mg levels are sufficient to inhibit classical growth *and* levels of carbonate ion accumulate rapidly to high values. If the saturation state reaches ACC solubility, the negligible free energy barrier to ACC formation allows for rapid precipitation of very high Mg ACC. This amorphous phase is thermodynamically unstable, and transforms to particles of VHMg calcite. However, subsequent growth of these particles is severely inhibited in the high Mg environments and the final products exhibit mesocrystal features as aggregates of nanoparticles with spherulitic and botryoidal textures.

4.1 Conceptual model

Combining results from this work and insights from previous studies suggests a process-based conceptual model for how geochemical conditions can bias pathways different types of calcite. The schematic diagram (Fig. 5) suggests a systematic, albeit qualitative, relationship between changes in the Mg : Ca conditions and saturation state through the supply of carbonate ion to produce calcite through three types of processes. In Field (1), low Mg environments combined with lower carbonate levels to produce calcite by the classical ion-by-ion addition process^{8,10,14,15} with compositions that reflect fractionation trends.

A second pathway is favored by the combination of moderate to high carbonate levels and higher Mg : Ca conditions (Field 2). Here, ACC is the initial precipitate and it subsequently transforms to HMg calcite with Mg contents up to 20 mol% MgCO₃. This composition range is reported for the skeletal structures of diverse calcifying organisms^{17,22,48–50} and also seen in some sedimentary environments.^{1,51}

Field (3) represents extreme settings that have high Mg conditions and a *rapid* increase in carbonate ion concentration to reach very high saturation states. The *combination* of these conditions is required to produce the very high Mg ACC that subsequently transforms to VHMg calcite (Field 3). At first glance, one might expect the highest Mg levels to favor aragonite, but we suspect the initial appearance of ACC and then calcite is a kinetic effect. That is, the rapid climb to high carbonate levels effectively ‘leapfrogs’ the aragonite field by reaching ACC saturation quickly. This favors precipitation of very high Mg ACC that (slowly) transforms by extensive nucleation to VHMg calcite. Subsequent growth of this calcite is severely inhibited by the high Mg levels to limit growth beyond the nanoparticle size range.

Finally, the conditions associated with the three qualitative fields in Fig. 5 suggest a geochemical window in the upper left portion of the diagram where calcite does not readily precipitate. This environment is associated with solutions that have high Mg

Fig. 5 Conceptual model for how the interplay of Mg : Ca ratio and carbonate supply bias pathways to CaCO₃ mineralization. When initial Mg : Ca ratio and saturation are low, calcite crystallites nucleate and grow by classical processes (Field 1). As Mg : Ca of the solution is increased, the growth rate of calcite slows to zero.^{8,14,42} There are two consequences of this inhibition: higher Mg : Ca levels in combination with a low supersaturation in carbonate level favor aragonite precipitation. However, higher Mg : Ca levels in combination with higher saturations promotes the rapid formation of a Mg-ACC that subsequently transforms to LMg to HMg calcites (Field 2) or, in the case of extreme environments, VHMg calcite (Field 3). The dashed lines denote the highly schematic nature of this illustration and serve as a reminder that the influence of geochemical factors such as inhibitors and pH are not considered here. **Annotations on the figure:** (a)^{5, 6} (b)⁷⁷ (c) *this study*.

levels but the carbonate supply is lower, or increased slowly to a level that is below ACC solubility. Previous studies indicate this region should favor aragonite because the calcite to aragonite transition is believed to occur at Mg : Ca ratios of approximately 0.9 to 2.0 in the laboratory^{5,6} and seawater,⁴ respectively.

To test this idea, we conducted additional experiments using a batch method with initial Mg : Ca ratios = 0.0 to 6.0 and carbonate levels that were insufficient to precipitate ACC.³³ Indeed, initial Mg : Ca > 2 produce 100% aragonite without evidence of calcite crystallites or nanoparticle aggregates (Fig. 6AB).

The diagram and experimental evidence, however, raise the point that multiple pathways to mineralization can emerge from a combination of kinetic and thermodynamic factors. Conditions that favor HMg and VHMg calcite *versus* aragonite provide good examples. Here, the local environment must 1) contain sufficient Mg to inhibit calcite growth through increased solubility—a thermodynamic factor; and 2) achieve a saturation with respect to ACC on a timescale that is shorter than the rate of aragonite nucleation—a kinetic factor. These insights provide a physical basis for the long-standing idea that the interplay between kinetic and thermodynamic factors govern patterns of carbonate precipitation in sedimentary environments.¹³

The conceptual model in Fig. 5 is consistent with previous field^{52–54} and laboratory studies^{5,6} that noted the importance of carbonate ion concentration as a primary control on the appearance of calcite *versus* aragonite. However, the construct is admittedly highly simplified and qualitative. The diagram does not account for the effects of minor and trace impurities on mineralization. For example, one would expect that Sr²⁺, large macromolecules or SO₄^{2–} could influence ACC formation or the stability of calcite *versus* aragonite (see later discussion). One could also ask why this conceptual model is different from the construct reported by Given and Wilkinson in 1985.⁵⁵ At that time, the scientific community had not recognized a low temperature pathway to classical growth of VHMg calcite. Moreover, it was not known that some aragonite ooids are likely deposited as ACC layers that transform to VHMg calcite (see later discussion) and are eventually altered to aragonite.

Fig. 6 Aragonite nucleation and growth is favored by the combination of high Mg : Ca levels and a slow saturation of the solution to values that are below ACC solubility.³³ ACC and aragonite are not observed to co-exist under any of the conditions investigated in this study. (A) Mg : Ca = 2.5 and (B) Mg : Ca = 4.5. Scale bar = 30 microns.

5. Implications

Insights from this study suggest the need to expand the traditional picture of how calcium carbonate minerals are formed to include the possibility of non-classical mineralization processes. Multiple pathways to carbonate precipitation may better explain some of the diverse patterns of carbonate deposition in the sediment record. Many questions are unanswered and need careful consideration to determine the scope of their importance.

5.1 ACC as precursor to disordered dolomite

The ability of the ACC pathway to produce VHMg calcite provides a possible explanation for the source of very high Mg carbonate needed to make disordered

dolomites at low temperatures.^{56,57} While disordered carbonates are proposed by a number of studies as possible precursors to ordered dolomite,^{58,59} the study shows the process by which calcite with very high Mg concentrations can precipitate. For a similar non-classical process to be generally applicable to the widespread occurrence of dolomite, the mechanism proposed here must also be able to operate over long periods of time in order to explain the volumes that are seen in the rock record. We suggest that diffusion boundary layers in pore systems or microbe–water interfaces are involved, where local, micron-scale environments can rapidly reach ACC saturation. Our findings support the idea that the precipitation of high and very high Mg calcite is favored in locally isolated or transport limited environments that allow Mg : Ca ratios to climb while also supplying high carbonate levels. This interpretation is consistent with that of Hardie,⁷ who proposed that both of these conditions are essential for dolomite formation and extensive field evidence that nearly all Proterozoic carbonates began as calcite or aragonite. Our findings also support anecdotal evidence that ACC formation is a key step *en route* to dolomite.^{56,58}

One field test of this concept is found in modern sedimentary dolomites from the Coorong Lakes, South Australia⁶⁰ that form in shallow evaporative waters with high Mg : Ca ratios of 5–50 and very high supersaturations.⁶¹ The disordered dolomites that occur in this geologically young sedimentary environment may provide an ‘evolutionary link’ to ordered dolomites in the rock record. Indeed, Coorong carbonates are 1–3 μm particles that express pseudo facets, yet are composed of co-oriented 50–200 nm particles that are consistent with the dolomite structure (Fig. 7A). SAED analysis shows these pseudofacets likely arise from partial ordering and co-alignment of the particles⁴³ (Fig. 7A inset). These features are comparable to the VHMg calcite produced in this study for sulfate-free (Fig. 7B) and sulfate-bearing (Fig. 7C) experiments that both exhibit some particle co-alignment (Fig. 7AB insets).

If disordered dolomites are indeed the products of an ACC to VHMg calcite conversion, then the rock record should contain evidence for their primary roots. Observations from this study suggest three plausible markers for origins in VHMg calcite that could be preserved in geological carbonates: first, some ancient carbonates may preserve relic structures of VHMg calcite as spherulites. For example, Proterozoic dolomites from Namibia show spherical structures⁶² that are similar to the VHMg calcite aggregates reported herein. Other spherules are seen in controversial reports of ‘nannobacteria’ that could be relic VHMg calcite.⁶³ Dolomite films or coatings that line the pore spaces of supratidal carbonates⁶⁴ could also result from repeated evaporations of sea water to form sheets of VHMg calcite similar to the low relief aggregates in this experimental study. Another possibility is carbonate mud, whose primary composition could conceivably have been ACC such as we hypothesize for the Coorong sediments. To explain the replacement of preexisting grains is, however, a more difficult challenge.

5.2 Other environments

Carbonate mineralization *via* ACC may also occur during the precipitation of ooids. As small coated grains, often <2 mm,¹ the origins of these spherical structures in carbonate platform environments have been debated for more than a century.^{65–67} Efforts to interpret ooid origins may have been complicated by observations of the aragonite that forms at later stages and because ACC formation was not recognized at the time. Some studies have also argued for a direct biological origin.⁶⁸ However, a recent analysis of individual layers that comprise natural ooids from the Bahamian Archipelago suggests each ‘overgrowth’ begins as a veneer of ACC that subsequently transforms to VHMg calcite.⁶⁹ This interpretation suggests ACC saturation can be readily achieved within a local microenvironment, likely as an indirect consequence of microbial activity to produce locally high levels of carbonate ions.

Fig. 7 SEM images of VHMg calcites produced in this study are similar to modern dolomitic carbonates. Natural and laboratory samples are comprised of aggregates of nanoparticles that possess some degree of interparticle co-alignment. All scale bars = 200 nm. (A) Modern dolomite from Coorong Lakes, Australia is comprised of 1–3 μM particles that express macro-facets consistent with termination. These particles possess partial ordering into 100–150 nm subdomains (inset). Individual particles are highly co-aligned along two predominant orientations along the [452] zone axis as seen in SAED spot patterns. (B) Calcites synthesized from control solutions at $\text{Mg} : \text{Ca} = 5$ are comprised of 58 ± 12 nm particles (35 mol% MgCO_3). (inset) Arcs in SAED patterns from synthetic samples indicate partial co-alignment of particles. (C) Sulfate solutions with initial $\text{Mg} : \text{Ca} = 5$ produce smaller 33 ± 6.8 nm calcite nanoparticles (45 mol% MgCO_3).

It appears likely that the formation of ACC in open marine environments of the modern ocean should be ruled out since both $\text{Mg} : \text{Ca}$ and oversaturation are thought to be buffered to moderate values. Thus, settings that allow local fluids

to evolve, such as in pore spaces associated with diagenetic environments or intertidal settings, may be most promising. In both of these situations, both Mg : Ca ratios and saturation state can become elevated as carbonate or gypsum (CaSO_4) precipitation occurs. The correlation of such environments with dolomite precipitation has been long recognized.^{70,71} Nevertheless, the mechanism proposed herein has an additional requirements: first, the reported solubility of ACC argues that ion concentrations be maintained or oscillate to high values relative to calcite saturation (*i.e.*, $>10\times$). Second, aragonite formation must be prevented. We show this can be achieved under conditions that supply a high carbonate level to favor the higher energy precipitation of ACC.

The botryoidal aggregates of calcite produced in this study bear a striking similarity to the larger scale (1–2 mm) carbonate botryoids that are seen in the Upper Cretaceous cements of many Mediterranean localities.⁷² These very high Mg calcites exhibit radial morphologies that were originally interpreted as aragonite. Low-relief botryoidal or “mound” structures are also noted as an intermediate morphology during the hydrothermal synthesis (218 °C) of dolomite.⁵⁸ However, the length scale of the individual nanocrystals (lateral dimensions of 10–200 nm) is consistent with the observations of this study. Though anecdotal, these observations suggest the origins of botryoidal carbonates with radial or botryoidal fabrics should be revisited. Almost nothing is known about how the ACC to calcite pathway influences the uptake of trace and minor elements beyond the marked changes in Mg fractionation reported herein. Finally, the influence of this pathway on isotopic signals is also unknown but synthetic disordered dolomites exhibit oxygen isotopes that are offset to significantly lower values than expected.⁵⁶

5.3 Biologically mediated carbonate formation

Microbial activity in sediments is widely recognized in carbonate mineralization. Generally, it is assumed that the extracellular polymeric matrix associated with biological processes directly modifies carbonate nucleation and growth.⁶² Alternatively, it has been shown microbial metabolic rates also directly control rates of carbonate mineralization.^{73,74} This relationship is implicitly contained in Fig. 5 through carbonate supply and the connection of this key variable to the many environmental parameters that control microbial metabolic rates (nutrient availability,⁷⁵ temperature,⁷⁶ metabolic process, *etc.*) and geochemical controls of cation concentrations. Their interactions, thus, have a strong influence on the pathway to carbonate mineralization.

In conclusion, the findings suggest the need to revisit the traditional picture of carbonate formation to consider non-classical pathways to mineralization and the consequences of interplays between kinetic and thermodynamic factors.^{7,13} A good example is seen in our observations that the very high Mg calcites are favored by a local environment that: 1) contains sufficient Mg to inhibit crystallite growth through increased solubility—a thermodynamic factor; and 2) achieves a saturation with respect to ACC on a timescale that is shorter than the rate of aragonite nucleation—a kinetic factor. For example, the intimate associations of calcite and aragonite that are observed in some cements⁵⁵ may be explained as the interplay of small fluctuations in the local geochemical environment. By revisiting the geochemical conditions that bias the energy landscape of mineralization toward different amorphous and crystalline phases, an updated view of relationships between mineralization patterns and environment may emerge.

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